

# 2005 DOE Hydrogen Program Development of Water Splitting Catalysts using a Novel Molecular Evolution Approach

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May 23<sup>rd</sup>, 2005

PDP38

This presentation does not contain any proprietary or confidential information

# Overview

## Timeline

- May 1, 2005
- April 30, 2009
- 0%

## Budget

- Total: \$1,500,000
  - DOE: \$1,200,000
  - Contractor: \$300,000
- FY04 funds: \$0
- FY05: \$500,000

## Barriers

Hydrogen Production

Barriers Addressed:

H. System Efficiency

P. Operating Temperature

## Partners

- Combimatrix,  
Mukilteo, Washington

## Objectives: Hydrogen Evolution Catalysts

- Develop a library-based solid-phase synthetic method for molecular evolution of a catalyst for electrolysis
- Evolve such a catalyst using metal binding peptide libraries based on photosynthetic complexes.
- Optimize the catalyst for minimum overpotential.

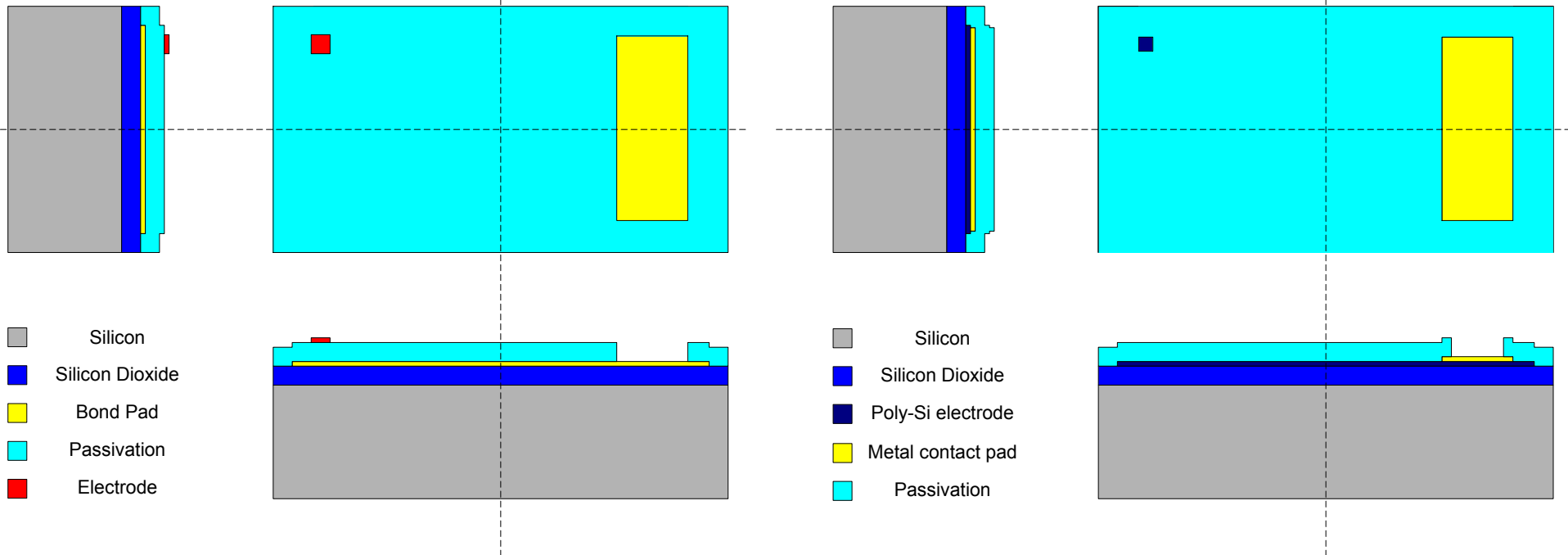
## Approach: Optically Directed Evolution

- Using a photosynthetic model system for oxygen evolution, design a peptide library
- Synthesize the library using photolithographic or electrochemical solid phase synthesis methods directly on an array of electrodes
- Measure the voltage/current characteristics of each catalyst, model the best, and design a new library, etc.

## Initial Accomplishments:

- Designed electrode elements and array structure.
- Designed initial guesses for metal binding peptide catalysts based on a photosynthetic model system.
- Set up micromirror array system and integration with a peptide synthesizer is in progress.
- Performed light directed synthesis of small peptide arrays.
- Developed relationship with Combimatrix to transfer technology to the lab for electrochemical synthesis of peptide arrays.

# Dual electrode design approach



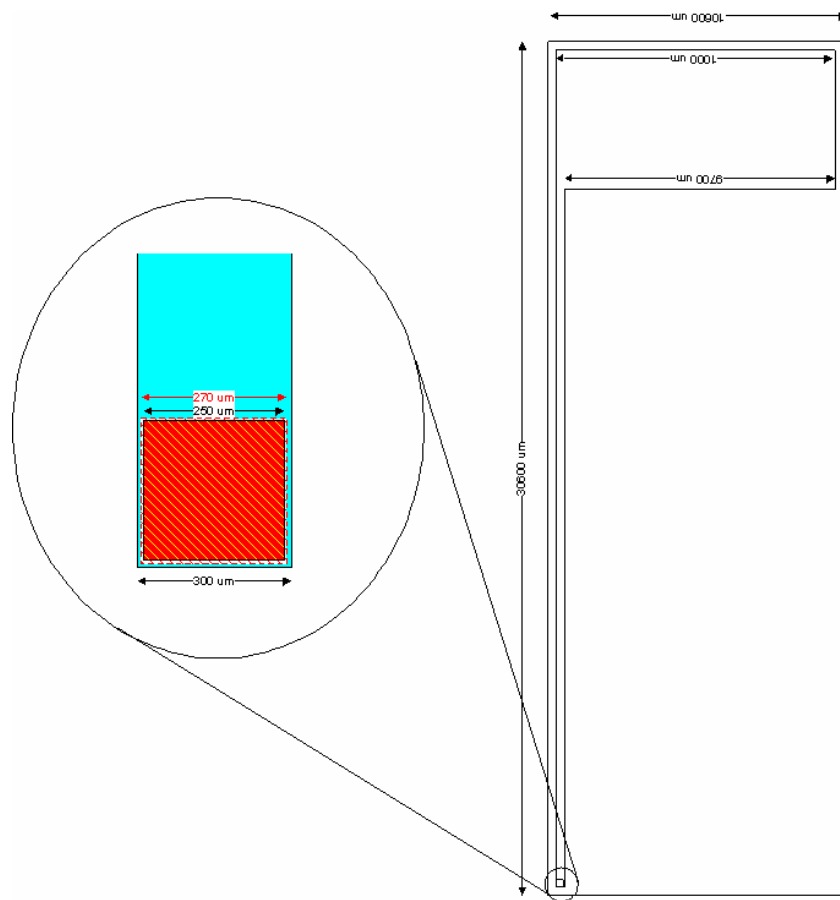
(a) Metallic electrode device schematic

(b) Poly-silicon electrode device schematic

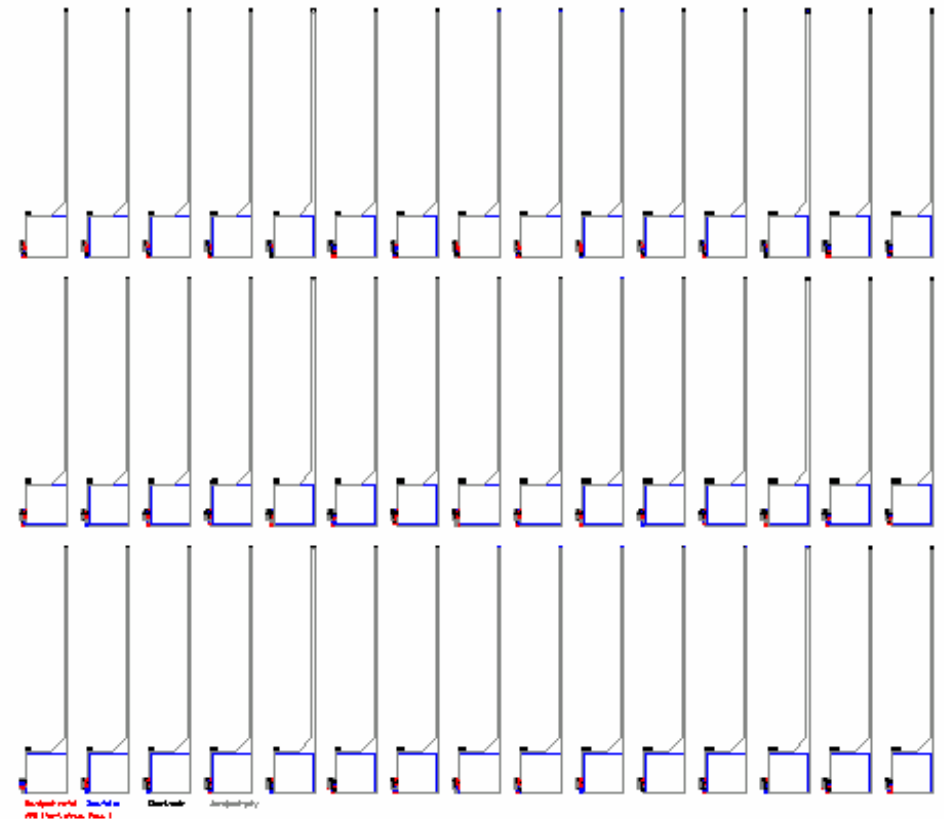
- Dual electrode design approach

- allows for attachment chemistries to both metallic and poly-silicon surfaces
- greater degree of freedom in device structure and design

# Schematic diagram of electrode array



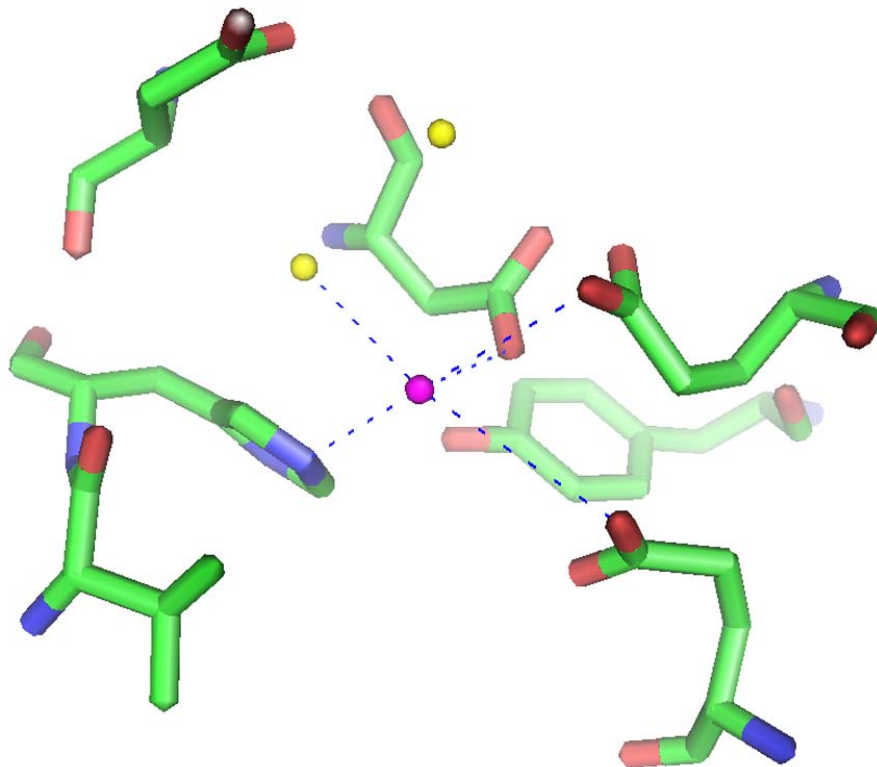
Individual electrode element. Electrode shown is 250 x250  $\mu\text{m}$



Array of electrodes with varying electrode area from 10 x 10  $\mu\text{m}$  to 250 x250  $\mu\text{m}$



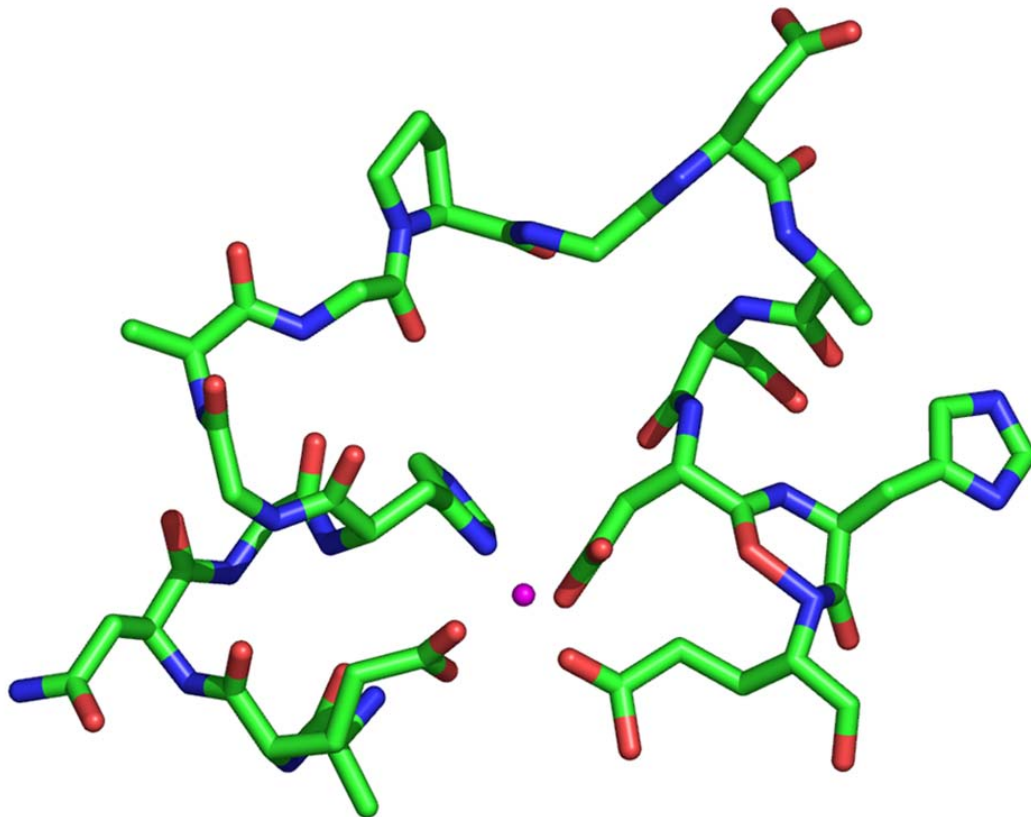
# The Reaction Center as a Model for Redox-Active Mn-Binding Peptides



- X-ray structure of an *Rb. sphaeroides* reaction center mutant engineered to bind a manganese and oxidize it upon light driven photosynthetic electron transfer.

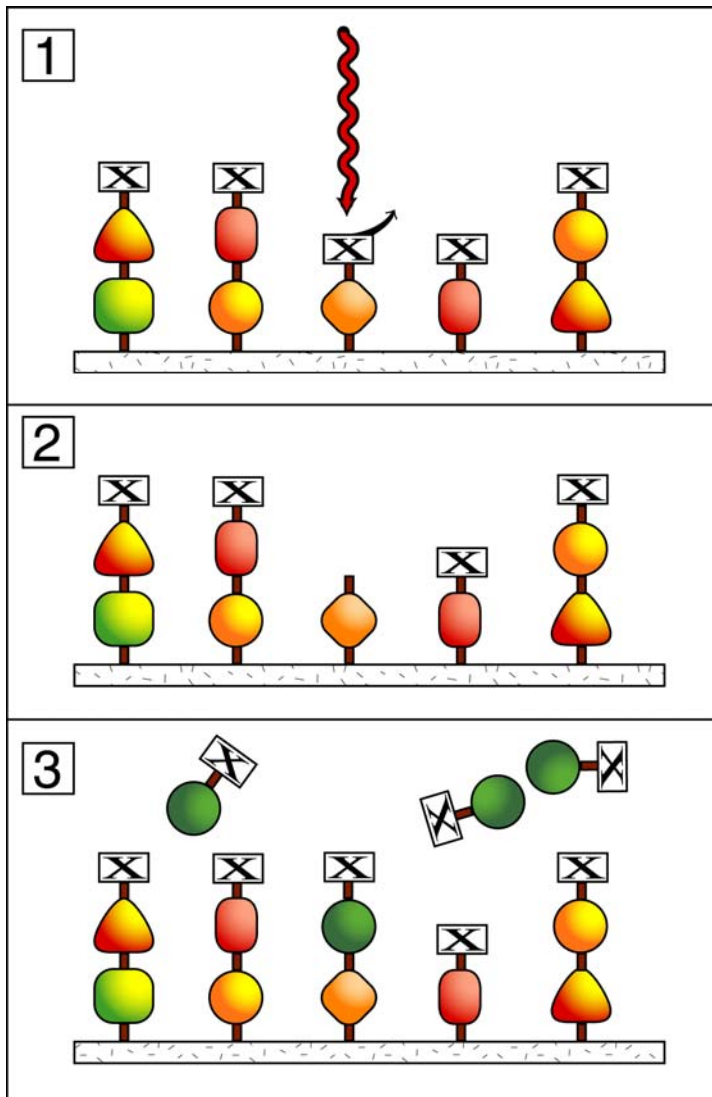


# Example Mn-Binding Peptide



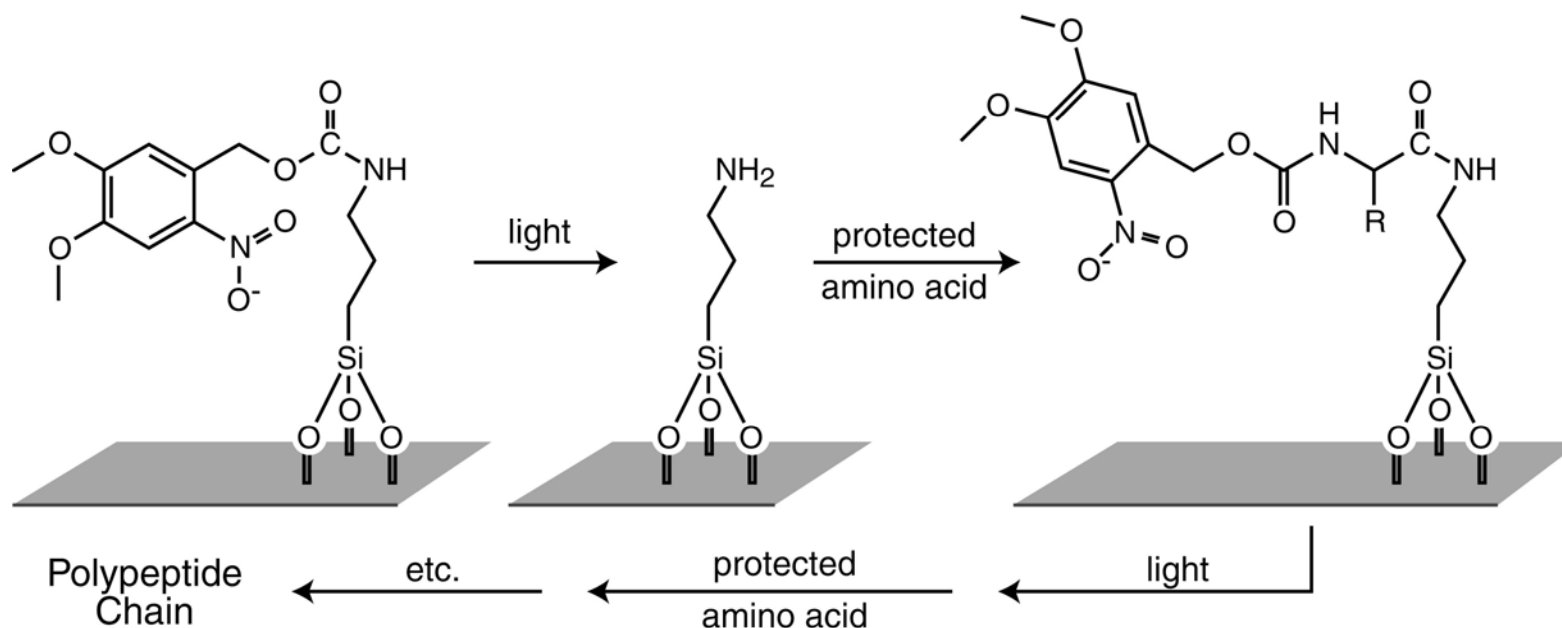
- Computer model of a Mn-binding polypeptide based on reaction center mutants made in Allen's lab. The peptide is 16 amino acids. The manganese is coordinated to two Glu, one His, and one Asp.

# Heteropolymer Synthesis using Light



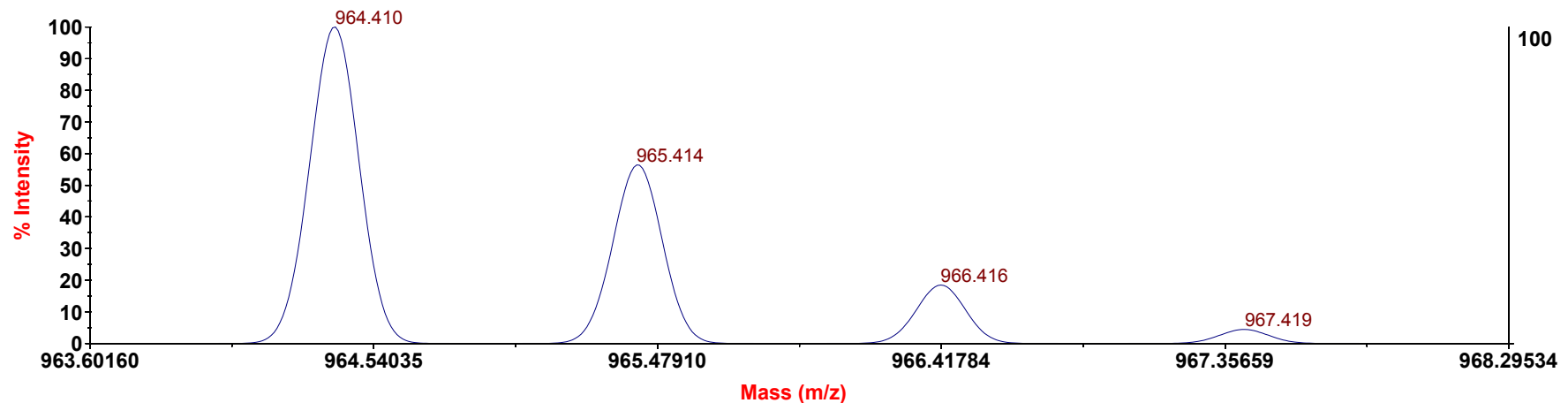
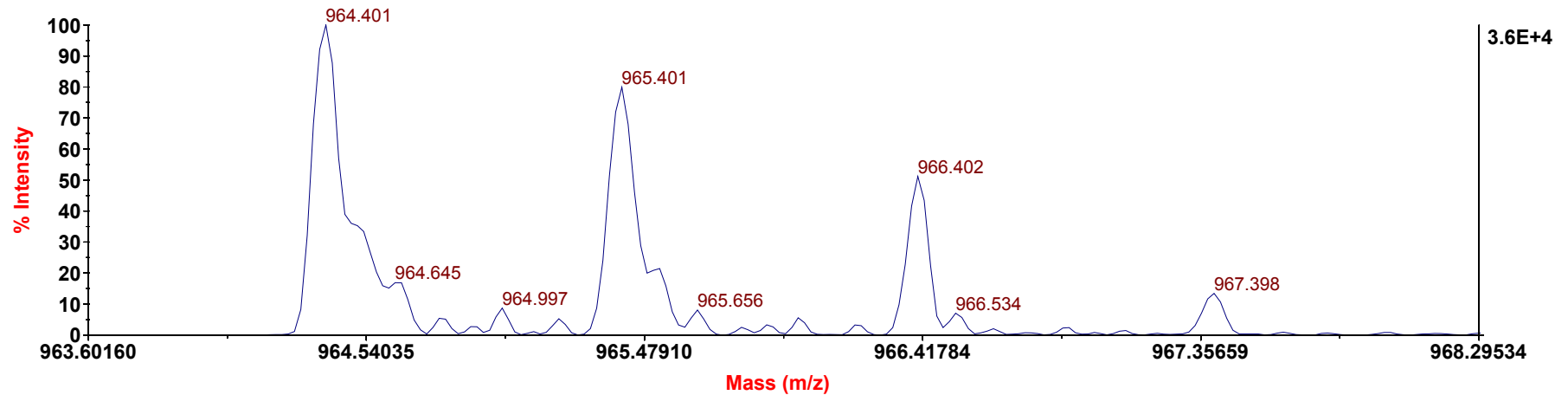
- Developed in early 90's and applied extensively to DNA Chip technology
- Photocleavable blocking groups removed in a patterned fashion by light.
- New monomer introduced only binds to illuminated regions

## Example Photochemistry

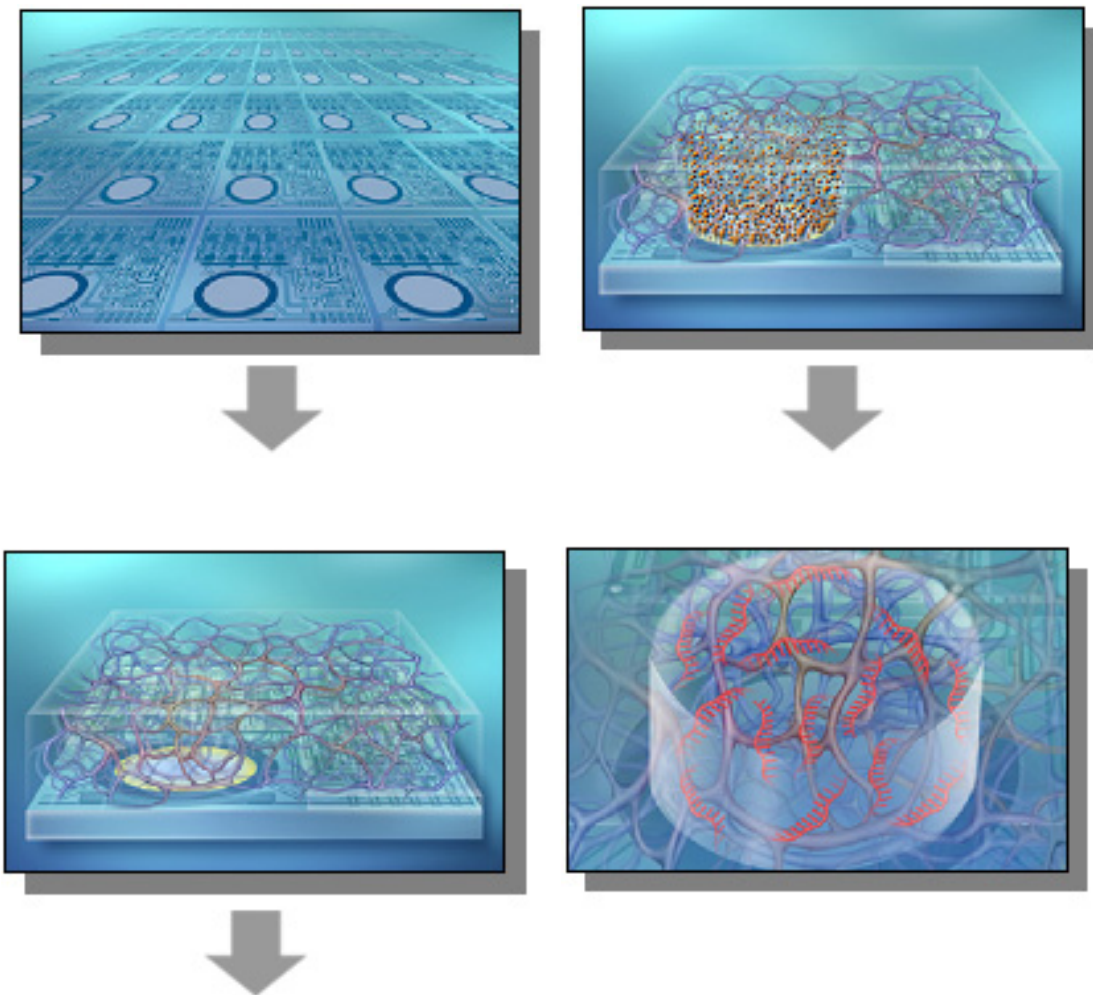


- Standard photochemical deblocking using NVOC
- There are a series of newer photocleavable groups that have been developed for the DNA chip industry that have higher yields and we are testing these.

# Mass Spec. of Small Peptide Made with Photolithographic Approach on Surface



Calibrated MALDI-TOF MS spectrum of observed isotopic distribution for the  $m/z=964.4$  Da ion vs. those predicted for the TMPP-GGFL [C<sub>48</sub>H<sub>63</sub>N<sub>5</sub>O<sub>14</sub>P] (bottom) .

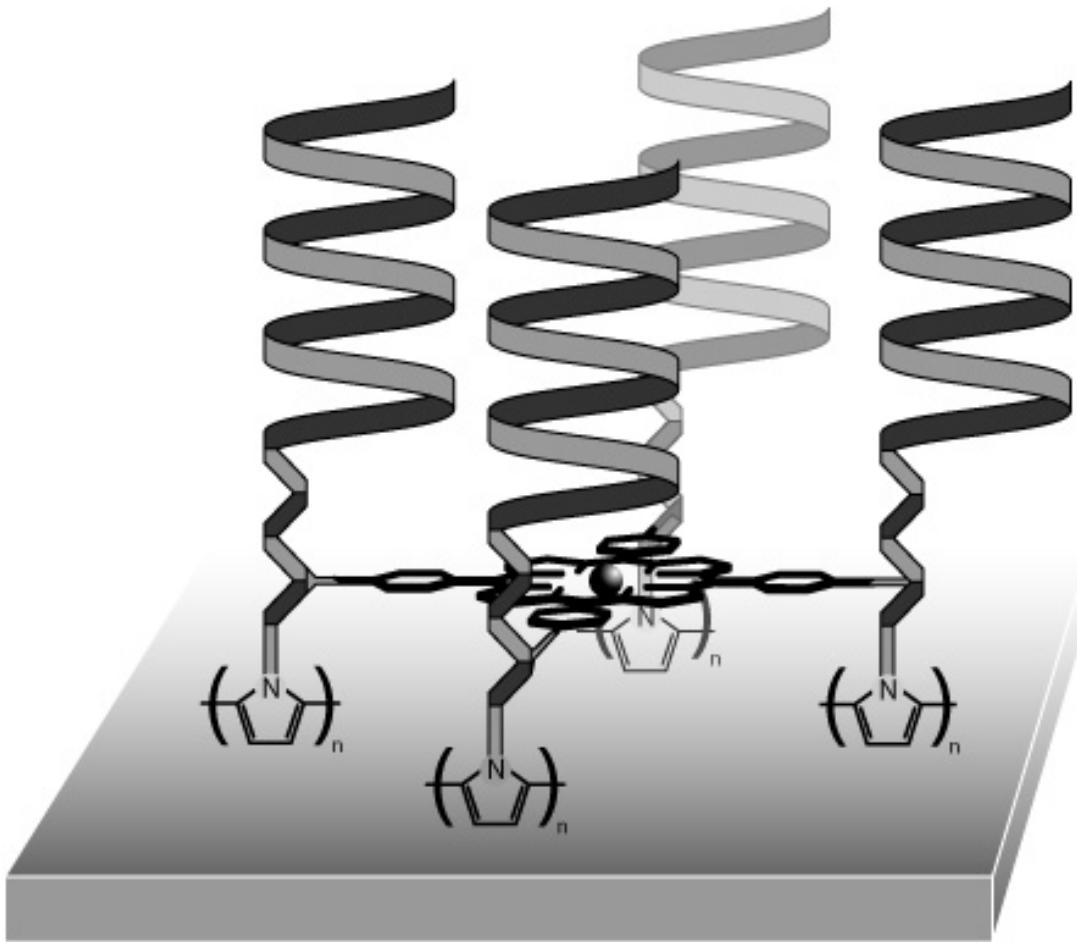


## Combimatrix Technology

- Developing collaboration with Combimatrix.
- They use electrochemistry to fabricate heteropolymers directly on electrodes.
- Are able to make arrays of 12,500.
- Already have electrochemical detection technology in place.



# Chemical Platforms for Molecular Evolution



- A variety of chemical platforms for catalyst evolution are being tested.
- These include both very simple monolayers of metal binding peptides are more complex helix bundle structures

## Future Work

- Synthesize and evaluate a series of initial test metal binding peptides
- Put these onto the newly designed electrodes and make initial electrochemical measurements
- Test the new photochemical blocking groups and optimize yields
- Transfer Combimatrix electrode technology into our laboratory
- Generate initial libraries of heteropolymers and perform electrochemical analysis.



# Publications and Presentations

Funding for this project is just arriving now. No publications based on that funding yet.

## Hydrogen Safety

This project results in negligible quantities of hydrogen produced. We are using very small electrodes and searching large libraries for catalytic activity. The hydrogen quantities produced are no more than a standard electrophoresis experiment. Hence, there are no hydrogen safety issues.